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Residues and Fate of Endosulfan on Field-Grown Pepper and Tomato

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Abstract: Endosulfan (Thiodan 3 EC), a mixture of α- and β-isomers, was sprayed on 92-day-old field-grown pepper and tomato at the recommended rate of 0·61 kg AI ha^{-1}. Plant tissue samples were collected at 1 h to 14 days after application and analysed to determine the content and dissipation rate of endosulfan isomers (α- and β-endosulfan) and the major metabolite, endosulfan sulfate. Analysis of samples was accomplished using gas chromatography-mass selective detection (GC-MSD). The results indicated the formation of endosulfan sulfate as a residue component on the plant tissues and also the relatively higher persistence of the β-isomer as compared to the α-isomer on pepper fruits. The initial total residues (α- and β-endosulfan isomers plus endosulfan sulfate) were higher on leaves than on fruits. On pepper fruits, the α-isomer, which is the more toxic to mammals, dissipated faster than the less toxic β-isomer. Total residues (α- and β-endosulfan isomers plus the sulfate metabolite) on tomato leaves revealed longer persistence ($t_{1/2}$ 4·6 days) compared to the total residues detected on pepper leaves ($t_{1/2}$ 2·0 days) 3–14 days following spraying. Persistence of the β-isomer on pepper fruits was high 3–14 days following spraying compared to on tomato fruits. This long persistence increases risk of exposure of the consumer. In addition, the longer persistence of the total residues on tomato foliage should be considered of importance for timing the safe entry of tomato harvesters due to the high mammalian toxicity of endosulfan. © 1998 Society of Chemical Industry

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Key words: Thiodan; endosulfan isomers; endosulfan sulfate; dislodgeable foliar residues; half-lives

1 INTRODUCTION

The demonstration of the effectiveness of a pesticide is not in itself sufficient to recommend it for commercial usage. A pesticide and/or its metabolites must be reasonably safe for those who apply its various formulations and it must leave no injurious residues on the edible portions of plants.[1–3]

Endosulfan, a mixture of α- and β-isomers (Fig. 1), is a broad-spectrum insecticide and is one of the remaining organochlorine insecticides registered in the USA for control of insect pests on fruits and vegetables.[4] Endosulfan has been employed extensively in agriculture and is one of the commonly used insecticides on

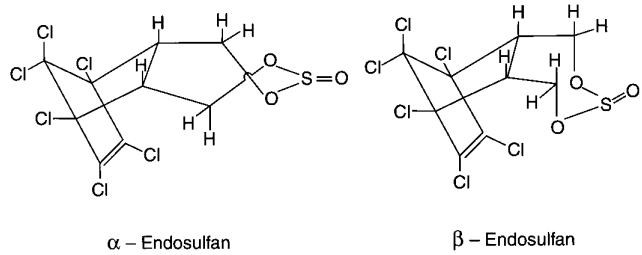

Fig. 1. Recently revised structures of α-endosulfan and β-endosulfan isomers. Structures are taken from Rice *et al.* (1997).[4]

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vegetables in Kentucky.[5] Upon reaching the surface of plants, endosulfan is capable of penetrating the epidermis.[6] It is, therefore, not a systemic insecticide but a residual insecticide[7] that acts as a contact poison on chewing and sucking arthropods. Endosulfan residues are detectable in crops at harvest time.[8] Although the transformation products of endosulfan, i.e. sulfate, diol, ether, hydroxy ether and lactone have been demonstrated,[6,9] only the sulfate (oxidation product of endosulfan sulfite) is significant as a residue component on plant surfaces.[10–16] Endosulfan and its sulfate are highly toxic to aquatic organisms, particularly fish,[8,17] and have been detected in water samples collected from the vadose zone[18] and in groundwater.[19] Therefore, the persistence of these compounds on the treated plant surface is of concern.

In 1991, the Codex Committee on Pesticides Residues requested updated data on the uses of endosulfan on forage and feed crops.[20] Recently, endosulfan has been reported to interfere in the spermatogenic[21] and steroidogenic cycle in adult rats[22] and has caused reduction in sperm count and alteration in sperm morphology.[23] Endosulfan sulfate was the only metabolite detected in the rat brain.[24] Table 1 shows some of the physical properties of endosulfan isomers and the sulfate metabolite that affect the persistence and behavior of endosulfan under field conditions.

A number of re-entry studies indicated that dermal exposure is usually the most important pathway by which pesticides enter a field worker's body.[29,30] The use of pesticides has been associated with many documented incidences of poisoning of agricultural workers who contact the plants or inhale dislodged residues during picking, stripping, thinning, pruning, and pinching crops[31,32] Establishing a re-entry period as a means of preventing exposure to pesticides allows toxic foliar residues to dissipate with time before workers come into contact with treated foliage.[3]

The present work was designed to determine the magnitude and dissipation rate of endosulfan isomers and their major metabolite, the sulfate, on two foliage and fruit surfaces (pepper and tomato) following a field spraying experiment, and to classify endosulfan residues as total residues (mass of insecticide per mass of plant tissues, $\mu g\ gm^{-1}$) to which consumers and/or insects may be exposed. In addition, we determined dislodgeable foliar residues (DFR) expressed as surface residues (mass of insecticide per unit leaf area, $\mu g\ cm^{-2}$) which are most available for dermal exposure and airborne loss and to which a field worker may be exposed.

2 MATERIALS AND METHODS

2.1 Spray treatments

The field study was conducted at the Kentucky State University Agricultural Research Farm, Franklin County. 36-Day-old plants were transplanted on 21 May 1993. Each plot ($n = 12$) was $3{\cdot}7 \times 22$ m and the experimental design was a 4×3 randomized complete block design with four treatments including the two crops (pepper and tomato) and two control treatments. Each treatment was replicated three times. Endosulfan 357 g $litre^{-1}$ EC ('Thiodan' 3EC) was applied once on tomato, *Lycopersicon esculentum* Mill. cv. Mountain Spring F_1 Hybrid and sweet pepper, *Capsicum annuum* L. cv. Bell Boy Hybrid on 16 July 1993 when tomato fruits became red ripe and pepper became mature green. The tomato canopy was almost three times higher than the pepper canopy. Spraying was carried out at a height of 15–20 cm above the plant canopy at the rate of 0·61 kg AI in a total volume of 157·5 litre of water ha^{-1} using a 4-gallon portable backpack sprayer (Solo) equipped with one conical nozzle operated at 40 psi (275 kPa). Maximum and minimum temperatures averaged 27 and 18·6°C, respectively with an average of 22·8°C during the experimental period. Rainfall was 1·0, 0·83, 0·41 and 0·28 cm on 16, 17, 18, and 26 July 1993, respectively. No other rainfall events during the experimental period were recorded by the KSU research weather station.

TABLE 1
Physical and Toxicity Properties of Endosulfan Isomers and its Sulfate Metabolite

Property	*α-Endosulfan*	*β-Endosulfan*	*Endosulfan sulfate*	*Reference*
Water solubility (mg $litre^{-1}$ at 22°C)	2·29	31·1	18·1	25
Vapor pressure (kPa at 20°C)	$6{\cdot}18 \times 10^{-6}$	$3{\cdot}24 \times 10^{-6}$	N/A[a]	26, 27
Melting point (°C)	109	213	181	8
LD_{50} Acute oral (rats, mg kg^{-1})	76	240	N/A	28

[a] N/A = Data not available.

2.2 Sampling procedure

Pepper and tomato fruits and leaves were harvested from treated plants and untreated controls at 1 h, 1, 3, 5, 7, 10 and 14 days following spraying. Samples of pepper and tomato fruits, 1–2 kg each, were collected at random from experimental plots for analysis for endosulfan residues. Unwashed fruits were quartered, subsamples from the opposite quarters were collected and kept frozen at $-18°C$ until extracted. Triplicate leaf samples, 100 g each, from each plot were collected randomly from the mid-canopy of plants 1 h prior to spraying and 1 h to 14 days post-treatment. A leaf punch, 2·2 cm diameter, was used to take 100 randomly selected leaf discs per sample. Samples were kept frozen at $-18°C$ until extracted.

2.3 Analytical procedure

In December 1993 (five months after sample collection), the frozen samples (0·5–1 kg of fruits) were macerated in a cutter-mixer and a 100-g subsample was blended for 2 min with methylene chloride [CH_2Cl_2] + acetone (6 + 1 by volume; 150 ml). After homogenization, the mixture was vacuum filtered through a Buchner funnel containing a glass microfibre filter paper, Whatman 934-AH, of 55 mm diameter (Fisher Scientific, Pittsburgh, PA). The resultant liquid was quantitatively transferred to a separatory funnel containing methylene chloride (50 ml) and sodium chloride solution (40 g litre^{-1}; 50 ml), followed by liquid partition for 1 min. The methylene chloride extract was passed through anhydrous sodium sulfate and concentrated by rotary vacuum evaporator (Buchi Rotavapor Model 461, Switzerland) to a known volume. Clean-up of residues was carried out on an open glass chromatographic column (20 × 1·5 cm) packed with 6 g silica gel + magnesium oxide (2 + 1 by mass).[33] The column was topped with a layer of anhydrous sodium sulfate (2 cm) and the adsorbent was first conditioned with hexane (50 ml), which was discarded. An aliquot of the concentrated extract was transferred to the column. The column was then eluted with acetone + hexane (20 + 80 by volume; 100 ml) which was collected in a 250-ml flask. The solvent was concentrated by rotary evaporator at 35°C. Final volume reductions to 1 ml of hexane were carried out under a stream of nitrogen gas.

Dislodgeable foliar residues (DFR) were extracted by agitating 100 leaf discs (collected using a leaf-punch of 2·2 cm diameter) with 100 ml of water containing 0·2 ml of 20 g litre^{-1} 'Tween'-20 for 20 min using a Multi-wrist shaker (Lab-Line Instruments, Inc., Melrose Park, IL, USA). This sampling procedure provided the same total surface area used for residue analysis for each type of foliage. The aqueous solution was extracted with 50, 25 and 25 ml of dichloromethane followed by filtration through Whatman 934-AH glass microfibre filter paper. The solvent was dried over anhydrous sodium sulfate, concentrated by rotary evaporator, and analysed by GC-MSD. The quantity of endosulfan detected in μg was divided by the surface area for 100 leaf discs to present the data in μg cm^{-2}.[34]

Alpha- and beta-endosulfan (6,7,8,9,10,10-hexachloro-1,5, 5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide) of >95% purity, and endosulfan sulfate (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro- 6,9-methano-2,4,3- benzodioxathiepin-3,3- dioxide), 99% purity were obtained from FMC Corporation (Agricultural Chemicals Group, Philadelphia, PA). Standards ranging from 0·35 to 6 ng μl^{-1} were prepared in hexane for GC-MSD injections and the unit areas were obtained using 1-μl injections. Linearity over the range of concentrations was determined using regression analysis. Standard solutions at 0·5 and 1 μg gm^{-1} levels were used to spike plant tissue samples for evaluating the efficiency of the analytical procedures used. Recoveries from the leaf surfaces were evaluated by applying to the leaf surface a mixture containing 1 μg of each isomer or the sulfate metabolite per cm^2 leaf area. One ml of the same mixture was added to the fruit homogenate in the blender to achieve a concentration of 1 μg of each isomer or the sulfate metabolite per g fruit.

Recoveries of endosulfan isomers and endosulfan sulfate from fortified fruit samples ranged from 93 to 96·2% for α-endosulfan, 89·6 to 91·5% for β-endosulfan, and 90 to 94·2% for the sulfate. Recovery values from fortified leaf samples were 92·9–94·3%, 87–90% and 91–96% for α, β, and the sulfate, respectively. All residue data have been adjusted for efficiency of recovery.

Residues were detected and quantified on a Hewlett–Packard (HP) model 5890A gas chromatograph (GC) equipped with a HP 5971 MSD operated in selective ion monitoring (SIM) and a HP 7673 automatic injector. The instrument was auto-tuned with perfluorotributylamine (PFTBA) at *m/s* 69, 219 and 502. The operating parameters of the GC were as follows: injector and detector temperatures 210 and 275°C, respectively. The oven temperature was programmed from 70 to 230°C at a rate of 10°C min^{-1} (2 min initial hold). Injections onto the GC column were made in splitless mode using a 4-mm ID single taper liner with deactivated wool. A 25 m × 0·20 mm ID capillary column containing 5% diphenyl and 95% dimethylpolysiloxane (HP-5 column) with 0·33 μm film thickness was used. The individual isomers were quantified by using SIM for the ions specific to these isomers, that is, 372, 406 and 408.[4] This method provided a minimum detection of 0·50, 0·35 and 0·75 ng for α-, β-endosulfan, and endosulfan sulfate, respectively and allowed the detection of endosulfan sulfate that contained the monitored ions with a dwell time of 100 msec. Helium was used as a carrier gas with 55 kPa column head pressure. The

mass spectrometer settings were electron impact ionization (EI) mode with 70 eV electron energy.

Quantification was based on average peak areas from two consecutive injections obtained from external standards ranging from 0·35 to 6 ng μl^{-1} prepared from each of the two isomers and the sulfate metabolite in hexane. Retention times of the α- and β-isomers and the sulfate metabolite were 24·81, 29·01 and 32·98 min, respectively. Residue data on plant tissues were used to calculate regression slopes and half-lives[35] for each of the three dissipation periods studied (1 h to 3 days, 3 to 14 days and 1 h to 14 days). Half-lives were analysed using analysis of variance (ANOVA);[36] Fisher's LSD was used to compare means.[37] Residues of endosulfan isomers, the sulfate metabolite, and total endosulfan detected were also analysed by crop type using ANOVA procedure. DT_{50} and DT_{90} values for α- and β-isomers were also calculated[38] and statistically analysed by crop species and plant tissue source.

3 RESULTS AND DISCUSSION

Commercial formulations of endosulfan contain two isomers and usually the α- isomer is more abundant than β-isomer.[4,15,39] The α-isomer is more volatile and less water soluble than the β-isomer (Table 1). Following a single application of 'Thiodan' 3EC at 0·61 kg AI ha^{-1}, residue levels of endosulfan on pepper and tomato declined over the 14-day study period. One h after spraying, the α-isomer was more abundant than the β-isomer on pepper fruits. Initial residues of α-endosulfan were 0·61 and 0·37 mg kg^{-1} on pepper and tomato fruits, respectively. Initial residues of β-endosulfan were 0·34 and 0·41 mg kg^{-1} on pepper and tomato fruits, respectively. Endosulfan sulfate was detectable in all fruit samples analysed (Fig. 2).

The Codex Committee on Pesticide Residues (CCPR) recommended a tolerance level of 2 mg kg^{-1} on vegetables and fruits.[40] The tolerances were to include residues of the two isomers (α- and β-endosulfan) and the metabolite endosulfan sulfate. On fruits, initial total residues fell below the tolerance level of 2 mg kg^{-1} 1 h after spraying and consisted primarily of the α- and β-endosulfan isomers while only traces of endosulfan sulfate were detected 1 h following spraying. Residues of the sulfate one week after spraying constituted 7·0 (±2·8)% and 6·2 (±1·5)% of total endosulfan on pepper and tomato fruits, respectively (Fig. 2).

Endosulfan initial residues on the leaves were higher than on fruits (data not shown). This is because of the difference in surface area between fruits and leaves for the same unit weight of sample and could be also due to the horizontal position of the lamina. Endosulfan initial residues were somewhat greater on tomato leaves than on pepper leaves (data not shown). This may be due to

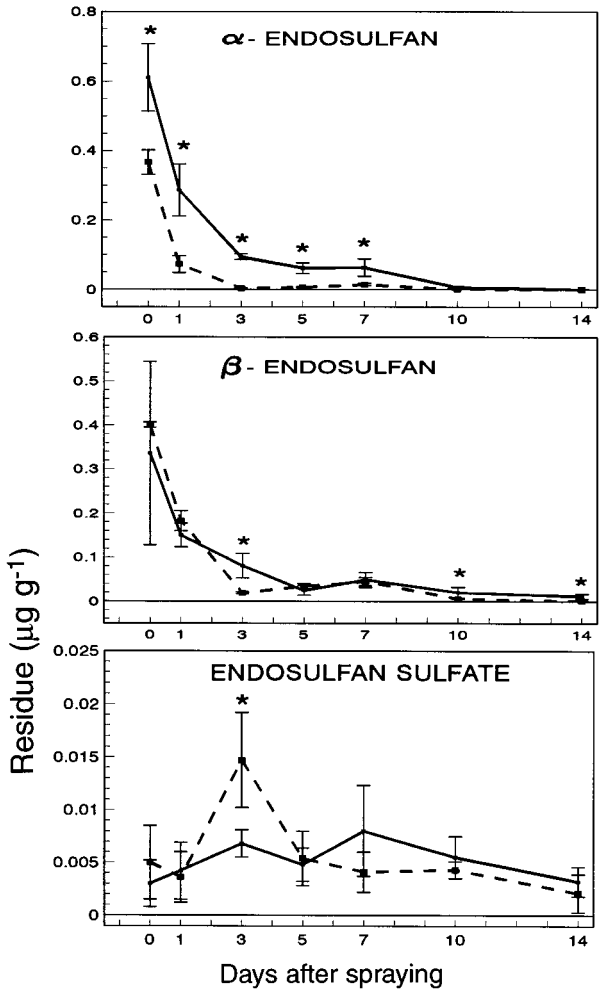

Fig. 2. Residues of α-endosulfan, β-endosulfan, and the major metabolite, endosulfan sulfate, on leaves following Thiodan 3EC application on (■) pepper and (■) tomato. Vertical bars indicate ±standard deviation; where no bar is shown it is less than the size of the symbol. Bars accompanied by asterisks indicate a significant difference ($P < 0·05$; Fisher's protected least significant difference test [SAS Institute 1991]) between the two crops at a given time.

the pubescent nature of tomato leaves compared to pepper leaves.

The dissipation of endosulfan residues following spraying indicated the relatively higher persistence of the β-isomer ($t_{1/2} = 3·3$ (±0·6) days) on pepper fruits as compared to the α-isomer ($t_{1/2} = 1·5$ (±0·1) days) during the experimental period (Table 2). Endosulfan sulfate, which is slowly degraded, both chemically and biologically,[41] was detected on the leaves and fruits as an oxidation product of the two sulfite isomers of endosulfan. The concentration of this transformation product fluctuated on the plant surface (Figs 2 and 3) and was not correlated with days after application of endosulfan. As a result, the formation and dissipation pattern of endosulfan sulfate on plant tissues during the experimental period could not be described by first-order kinetics. Endosulfan sulfate is formed from the transformation of α- and β-isomers, which have different

TABLE 2
Half-Lives of α-, β-Endosulfan, and Endosulfan Sulfate on Field-Grown Pepper and Tomato Following 'Thiodan' 3EC Spraying (Kentucky State University Agricultural Research Farm, Franklin County, 1993)

Period used for calculations (days)	*Half-life ($t_{1/2}$; days)*[a]					
	α-Endosulfan		*β-Endosulfan*		*Total (α+β+SO_4)*	
	Pepper	*Tomato*	*Pepper*	*Tomato*	*Pepper*	*Tomato*
			Fruits			
0–3	1·1 (±0·1)**	0·5 (±0·0)	1·8 (±0·7)*	0·7 (±0·0)	1·3 (±0·2)*	0·7 (±0·1)
3–14	1·5 (±0·2)$^{N.S.}$	2·8 (±0·9)	4·9 (±1·7)**	2·2 (±0·6)	3·1 (±0·4)$^{N.S.}$	2·8 (±0·7)
0–14	1·5 (±0·1)$^{N.S.}$	1·7 (±0·3)	3·3 (±0·6)*	1·8 (±0·3)	2·5 (±0·2)$^{N.S.}$	2·0 (±0·3)
			Leaves			
0–3	0·6 (±0·1)$^{N.S.}$	0·8 (±0·0)	0·9 (±0·1)$^{N.S.}$	0·8 (±0·1)	1·0 (±0·1)$^{N.S.}$	0·9 (±0·1)
3–14	3·0 (±1·7)$^{N.S.}$	3·5 (±0·8)	1·8 (±0·5)**	4·1 (±1·3)	2·0 (±0·4)**	4·6 (±1·3)
0–14	1·6 (±0·4)$^{N.S.}$	2·0 (±0·3)	1·5 (±0·2)$^{N.S.}$	2·3 (±0·4)	1·7 (±0·2)*	2·6 (±0·4)

[a] Each value is an average ± standard error of three independent replicates per treatment. Note that statistical comparisons were done between the two crops for each sampling period for each parent isomer (α or β) or total endosulfan. Total values refer to $t_{1/2}$ calculated from combined concentrations of the two parent isomers (α and β) plus endosulfan metabolite (the sulfate). Significances of LSD test between the two crops for each parent isomer or total endosulfan are given in superscript; *, $P < 0·05$; **, $P < 0·01$; N.S. not significant ($P > 0·05$).

and irregular behaviors for conversion to the sulfate.[16] Data presented in Figs 2, 3 and 4 indicated that dissipation of endosulfan on pepper and tomato plants has two dissipation phases. The first phase, a rapid dissipation phase, occurred from 0 to 3 days after spraying, then the rate of dissipation during 3–14 days was slower. In addition to weather conditions that affect pesticide persistence on plants, the rate at which a crop grows greatly influences the apparent persistence of pesticide residues on the leaves and other parts because residues become diluted by a greater surface area as the plant grows.

The overall half-lives for each of the two isomers and total endosulfan for each of the two consecutive first-order kinetic phases (0–3 and 3–14 days) and for the overall experimental period (0–14 days) are given in Table 2. Correlation coefficients between concentration and time after application were significant ($r > 0·90$) for all periods for total endosulfan and for the two isomers. Better correlation coefficients were obtained when the dissipation was fitted to two linear phases; the initial (0–3 days) with a shorter half-life, and the later phase (3–14 days) with a longer half-life and a lower degradation constant.

The results in Table 2 indicated that the β-isomer of endosulfan was generally more persistent than the α-isomer. This was especially apparent for pepper fruit. DT_{50} and DT_{90} values were also calculated for each of the two isomers and for total endosulfan during the experimental period. DT_{50} values were significantly different for the two isomers over crops and plant tissue sources (1·5 (±0·28) days for the β-isomer and 0·90 (±0·08) days for the α-isomer). These findings supported the conclusion that, in this experiment, the β-isomer was more persistent than the α-isomer. However, the average DT_{90} values for each of the two isomers were not significantly different (3·1 (±0·13) days for the β-isomer and 2·9 (±0·06) days for the α-isomer).

Dissipation of total residues at any time interval following spraying was higher on tomato fruits than on pepper fruits (Fig. 4). Half-lives on pepper fruits during the early dissipation phase for the α- and β-isomers were about twice those on tomato fruits. DT_{50} values for the β-isomer were not significantly different ($P > 0·05$) for pepper fruits (1·76 (±0·90) days) and tomato fruits (0·92 (±0·53) days). Likewise, the DT_{50} values for the α-isomer were not significantly different ($P > 0·05$) for pepper fruit (1·03 (±0·22) days) and tomato fruit (0·62 (±0·02) days). However, DT_{90} values for the β-isomer were significantly higher ($P < 0·0001$) for pepper fruits (3·8 (±0·27) days) than for tomato fruits (2·8 (±0·01) days). DT_{90} values for the α-isomer also were significantly higher ($P < 0·0001$) for pepper fruits (3·2 (±0·07) days) than for tomato fruits (2·7 (±0·002)). These differences may be explained by the smooth and spherical surface of tomato fruits compared to pepper fruits and could also be due to different cuticular wax composition, different thickness of wax deposition or more cracks in the cuticle of pepper fruits compared to tomato fruits. In addition, solubilized materials such as emulsifiable formulations are washed off easily following rainfall[42] especially from rounded surfaces like tomato fruits.

Dislodgeable foliar residues (DFR) of the sulfate metabolite, the oxidation product of the two sulfite isomers, expressed as μg cm^{-2} on pepper leaves were

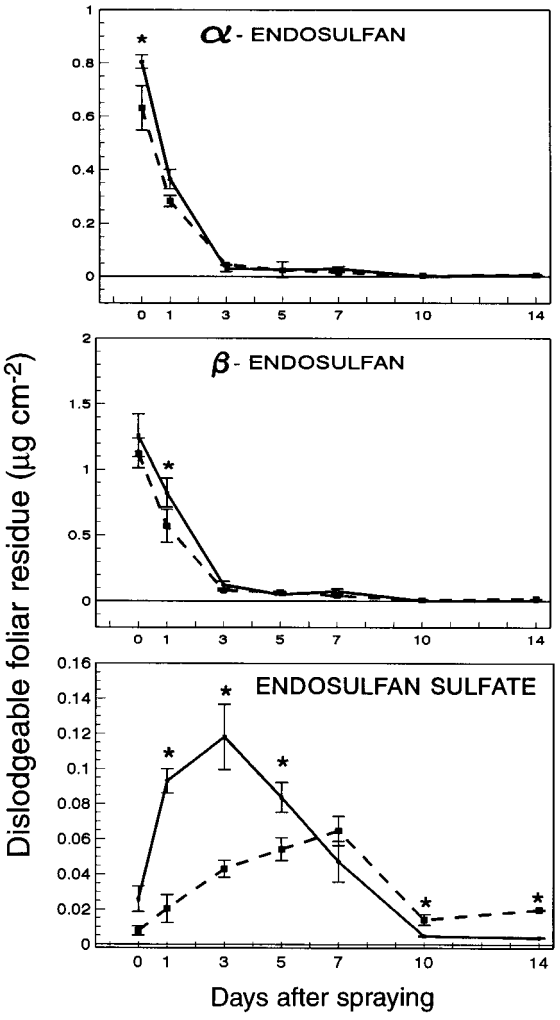

Fig. 3. Dislodgeable foliar residues (DFR) of α-endosulfan, β-endosulfan and concentration of the major metabolite, endosulfan sulfate, on leaves following Thiodan 3EC application on (■) peppers and (■) tomato. Vertical bars indicate ± standard deviation; where no bar is shown it is less than the size of the symbol. Bars accompanied by asterisks indicate a significant differences ($P < 0{\cdot}05$; Fisher's protected least significant difference test [SAS Institute 1991]) between the two crops at a given time.

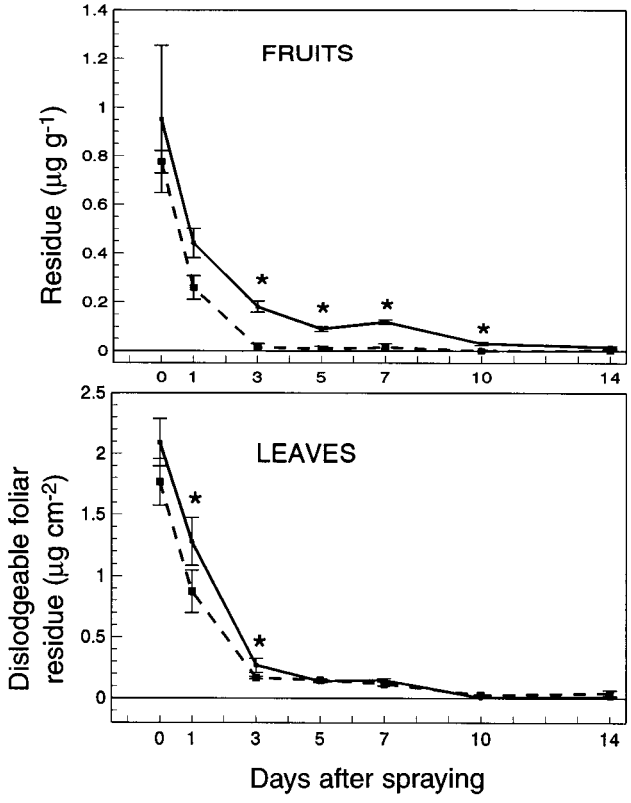

Fig. 4. Total endosulfan residues (α- and β-isomers plus the sulfate metabolite) on fruits (upper graph) and total endosulfan residues on leaves (lower graph) following Thiodan 3EC application on (■) pepper and (■) tomato. Vertical bars indicate ± standard deviation; where no bar is shown it is less than the size of the symbol. Bars accompanied by asterisks indicate a significant differences ($P < 0{\cdot}05$; Fisher's protected least significant difference test [SAS Institute 1991]) between the two crops at a given time.

significantly higher than those detected on tomato leaves 1–5 days after spraying (Fig. 3). DFR of the total endosulfan residues on pepper leaves were also higher than those detected on tomato leaves 1–3 days after spraying (Fig. 4, lower graph).

The fate of the α- and β-isomers varies, and the observed ratio of the isomers in the environment is dependent upon the physical state of environmental compartments.[39] Some researchers have observed substantial conversion of the β-isomer to the α-isomer and little concomitant conversion of α to β.[4,25,43] The environmental half-life of the β-isomer has been shown in some studies to be shorter than that of the α-isomer.[4,25,27,43] Our experiment was not designed to allow us to evaluate interconversion between α- and β-isomers. However, our results support the concept that the greater volatilization of the α-isomer from solid surfaces as well as aqueous systems,[43] compared to the β-isomer, has a great impact on its dissipation. Endosulfan with its two isomers is, in fact, two insecticides with different water solubilities and volatilities.

The persistence and degradation studies of endosulfan isomers in carnation plant (*Dianthus caryophyllus* L.) grown under greenhouse conditions revealed that the half-life ($t_{1/2}$) of the β-isomer was greater than that of the α-isomer.[16] Studies on the dissipation of endosulfan isomers on chickpea under field conditions[15] indicated that the α-isomer was converted to the β-isomer in minor quantities, while it was converted into endosulfan sulfate on chickpea leaves in significant amounts. The α-isomer dissipated with time, with 98·4% lost in 15 days. Although endosulfan sulfate was present in the same amount as the β-isomer in harvest pod covers, no α-isomer was detected in harvest grains or pod covers. Our study on pepper and tomato also revealed that the β-isomer is more persistent than the α-isomer. Other workers have also reported that the α-isomer dissipated more rapidly than the β-isomer of endosulfan.[44,45]

Pepper is a perishable crop which must be harvested frequently and regularly. Insecticides having long post-application waiting periods are not compatible with vegetable production.[2] Consequently, the use of endosulfan on pepper under a wide range of production systems and multiple sprays should be kept to a minimum due to the long persistence of its β-isomer on the fruits. Pepper is normally marketed and consumed as fresh fruit. Endosulfan residues detected on pepper fruits (0·95 $\mu g\ g^{-1}$) were the result of only a single application of 'Thiodan' 3EC. Endosulfan residues on treated pepper fruits may exceed the tolerance level of 2 $mg\ kg^{-1}$ under intensive agricultural use where endosulfan is recommended on a two-week schedule[5] for control of many vegetable insects.

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